BORON NITRIDE

BY A. A. GIARDINI

Information Circular 7664

UNITED STATES DEPARTMENT OF THE INTERIOR
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Work of this Bureau manuscript completed March 1953.

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August 1953

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A. A. Giardini[1]

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INTRODUCTION

This report represents the results of a literature study on boron nitride and related substances. The purpose of the study was to find information that might be of value for production of a new, hard modification of boron nitride-preferably in single crystal form.

The report consists of a review of the major developments in boron nitride research, a discussion of the results, tabulations of physical and chemical properties, conclusions drawn from the study, and a bibliography.

PREVIOUS RESEARCH (PRIOR ART)

1842

Boron nitride was prepared for the first time by Balmain (1, 2, 3)[2] He reported two forms of the compound. He first believed that the product of the reaction was analogous to cyanogen, which then combined with the metals to form compounds similar to the cyanides. He named them the aethonides. Later, he realized that his aethonides were compounds of boron and nitrogen. One form was unalterable by white heat but was decomposed by treatment with water at normal temperatures and did not phosphoresce before the blowpipe. The second form was not decomposable by any reagents except water and oxygen at high temperatures, and it phosphoresced before the blowpipe. To form boron nitride, he heated mixtures of the following: Boric acid and melon;[3] 12 parts mercuric cyanide, 1-1/2 parts boric acid, and 1 part sulfur; potassium cyanide and molten boric acid.

1850

Wöhler (4) prepared boron nitride by heating a mixture of borax and ammonium chloride.

1857

Wöhler and Sainte-Claire Deville (5) formed boron nitride by heating amorphous boron in a stream of dry ammonia and by heating amorphous boron or a mixture of boric acid and carbon (the latter in an amount sufficient to reduce the boric acid) in a stream of nitrogen. A white boron nitride was produced, which was decomposed by caustic potash.

1859

Martius (6) produced boron nitride by heating boron ammino-trichloride.

2/ Underlined numbers in parentheses indicate references in the bibliography.
3/ $C_6H_3N_9$ - Webster's New International Dictionary, 2d ed., 1941.

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1869

Darmstadt (7) formed boron nitride by heating a mixture of boric acid and urea.

1892

Moissan (8) reported that amorphous boron would unite with nitrogen to form boron nitride at 1,200° C.

1901

Stock and Blix (9) obtained pure boron nitride by heating boron imide ($B_2(NH)_3$) and boron imidochlorohydrate at 130° C. Analysis showed the nitrogen content to be 55.6 percent. It was easily decomposed by boiling water.

Vournasos (10) reported forming boron nitride by heating boron in hydrogen cyanide or cyanogen.

1902

Moeser and Eidmann (11) found that by heating a mixture of 1 part finely powdered boric acid with 2 parts pure tricalcium phosphate in an atmosphere of ammonia in a gas-blast oven, an 80-90 percent yield of boron nitride was obtained. The inert phosphate acted as a porous carrier for the boric oxide and thus permitted a greater degree of gas diffusion and nitrification. After the nitriding reaction was completed the phosphate was dissolved with hot, dilute hydrochloric acid and the boron nitride residue washed with water. The product was a white, nonmelting, amorphous, voluminous powder, which phosphoresced when heated by a gas flame. It decomposed slightly in cool water and slowly in boiling water. The boron nitride analyzed 47.6 to 53.8 percent nitrogen.

1908

Stock and Holle (12) produced boron nitride by heating boron aminobromide.

1913

Heyder (13) made boron nitride by heating a powder mixture of 2 parts boric anhydride, 1 part magnesium, and 3 parts ammonium chloride. The mixture was heated to a temperature of about 300° C. to initiate the exothermic reaction, the temperature of the mass then being raised to about 800° C., whereby nitrification occurred. The magnesium impurities were dissolved with dilute sulfuric acid, and the boron nitride was washed with water, then alcohol, and dried in vacuo at 60°-70° C.

Stahler and Elbert (14) reported that they produced boron nitride by reducing B_2O_3 and $CaB_4O_7 \cdot 4H_2O$ with carbon in an atmosphere of nitrogen.

The British Thomsom-Houston Co., Ltd. (15), patented a method of producing stable boron nitride. It consisted of heating a mixture of a boron compound (for example, borax or boric anhydride) and a cyanide (for example, potassium or sodium cyanide) to a temperature at which reaction occurred (about 2,000° C.) and continuing the reaction until products other than boron nitride were volatilized. About 30 percent and upward of the theoretical yield of white, stable boron nitride was realized.

1915

Weintraub (16) obtained a patent on a process identical to that of the Thomson-Houston Co. He (17) also patented a process for converting chemically unstable boron nitride to a stable modification that is unaffected by water and oxygen at elevated

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temperatures. The procedure consisted of adding about 20 percent borax, boric anhydride, or other boron compounds volatile at the temperature of the treatment and heating the mixture to about 2,000° C. The boron nitride was surrounded by a protective atmosphere of the volatile fumes, which suppressed its decomposition. The heat treatment was continued until no more fumes were evolved.

1917

Podszus (18) reported a method of forming ceramic bodies of pure, stable boron nitride. A 66 percent B_2O_3 + 34 percent BN powder mixture was thoroughly mixed with a binder, such as paraffin, and warmed to 40° or 50° C. to form a plastic mass for shaping the body; it then was sintered. The final temperature depended on the water content and particle size. Material of 1-2 microns was completely sintered at 800° C. The ceramic body then was treated with ammonia gas at 1,000° C. for 30 to 40 hours and then at 1,300° to 1,400° C. for 3 hours. The smaller the particle size, the slower was the gas diffusion and therefore nitrification.

1919

Lindblad (19) developed an electric furnace for producing nitrides. It consisted of an inverted frustoconical chamber having an axially disposed inlet at the upper end into which a charge of boric acid and carbon was admitted. Electrodes extended into the chamber between the side walls. A bottom inlet was provided for blowing nitrogen or nitrogenous gases into the reaction chamber. A temperature of about 2,000° C. was suggested as the operating temperature.

Slade and Higson (20) determined the dissociation pressure of boron nitride. The equilibrium (of the type $2B + N_2 \rightleftarrows 2BN$) was found by heating small quantities of the metal (contained in a platinum tube) to a known temperature, introducing nitrogen into the furnace, and determining the value to which the pressure fell. The nitrogen was then pumped out and the equilibrium established from the low-pressure side. At 1,240° C. the nitrogen pressure dropped to 9.4 mm. and seemed to be approaching 9 mm. when the boron attacked the platinum tube, causing it to leak. At 1,222° C., where the nitrogen pressure was not greater than 9.4 mm., the heat of formation, as calculated from the Nernst equation, was about minus-69,000 calories, or minus-34,500 calories per mole.

1920

Tiede and Buscher (21) investigated luminous boron nitride. Samples of boron nitride were produced by (a) heating boric acid and a cyanide to 1,200° C., (b) heating boric acid and urea, (c) heating borax and ammonium chloride, and (d) thermal decomposition of boron trichloride and ammonia. They found that nonluminous boron nitrides were virtually pure, whereas those that luminesced under the influence of various test flames contained an impurity of B_2O_3. The B_2O_3 was considered as a luminescing flux, and the phenomenon was classed as one of a physical nature.

1921

Meyer and Zappner (22) devised a process for producing a 99.4 percent pure, white boron nitride, yields of which were 80 percent of the theoretical. It involved the thermal decomposition of a mixture of boron trichloride and ammonia in a vertical quartz tube electrically heated in such a manner that a 500° - 600° C. initial temperature and a final temperature of 1,000° C. was maintained. Provision was made for continuous removal of the ammonium chloride formed in the reaction.

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1923

Peacock (23) patented a process for producing boron nitride by heating boric anhydride in nitrogen to about 300° C. At this temperature metallic sodium was added to the oxide, and an exothermic reaction occurred; the temperature of the reaction was kept at 800° - 1,000° C. by controlling the sodium feed. The sodium oxide formed was then distilled from the BN at about 1,100° C.

Böeseken (24) pointed out the crystallographic possibility of a hard, diamond-type crystal structure for boron nitride.

1924

Jevons (25) proved that the band spectra, which he had observed in the flame produced by the action of active nitrogen on boron trichloride, were those of boron nitride and not those of boron oxide (BO) as Mulliken (26) had assumed.

1925

Tiede and Tomaschek (27) were able to show that carbon alone was the activating element of luminescent boron nitride (compare Tiede and Buscher (21) 1920).

Friederich and Sittig (28) obtained a pure, stable boron nitride by heating a mixture of anhydrous boric oxide and lampblack packed in a porcelain tube to a temperature of 1,250° C. in a current of pure, dry nitrogen.

1926

Grimm and Sommerfeld (29) noted that theoretically boron nitride can have a crystal structure similar to that of the diamond.

Goldschmidt (30) investigated the crystal-chemical relationship between boron nitride and carbon (graphite). To obtain single crystals suitable for his work, he bombarded a pressed capsule of amorphous boron nitride with cathode rays. By this treatment a temperature of over 2,500° C. was obtained and the powder recrystallized, giving small hexagonal plates 0.001 to 0.003 mm. in diameter. From these he was able to measure various optical and physical data and establish the close relationship to graphite. Hassel (31) was asked to carry out an X-ray investigation of the material and found that the crystal structure of Goldschmidt's recrystallized boron nitride was similar to that of graphite. One of every two carbon atoms was substituted for by a nitrogen atom and the other by a boron atom. The axial demensions were given as $\underline{a} = \sqrt{3} \times 2.51$ A., $\underline{b} = 2.51$ A., $\underline{c} = 6.69$ A., and $\underline{c}/\underline{a} = 1.54$. The possible space groups were C_{3i}^{1}, C_{3v}^{4}, D_{3}^{2}, D_{3d}^{2}, D_{3h}^{4}, C_{6}^{6}, C_{6v}^{4}, C_{6h}^{2}, D_{6}^{6}, and D_{6h}^{4}.

Montemartini and Losana (32) reported that boron (96.75 percent pure) when heated to 1,050° C. in various dry mixtures of oxygen and nitrogen formed no boron nitride when the nitrogen content of the gaseous mixture was under 70 percent. However, 95.2 percent of the boron was converted to boron nitride in a dry mixture containing 99.4 percent nitrogen.

1928

Lorenz and Woolcock (33) investigated the decomposition pressure of boron nitride between 1,695° and 2,045° C. The heat of formation calculated per mole of BN was minus-28,100 calories (compare Slade and Higson (20) 1919).

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1933

Podszus (34) found that the degree of electrical conductivity of boron nitride depended upon the type of surrounding gas, the period of heating, the vacuum pressure, and the structure of the nitride. Recrystallization led to a considerable reduction in conductivity. In gases that corresponded to the anion, the conductivity was less; in a reactive gas, such as hydrogen, the conductivity was greater. The conductivity decreased with increasing energy of formation. The more completely the conductivity could be represented by a single e function (from the formula $k_{(\text{conductivity})} = Ae^{-\frac{B}{T}}$), the purer was the substance. The values for the constants A and B were found to be (a) in a vacuum, A = 1.5 x 10^{22} and B = 104,000; (b) in nitrogen, A = 3 x 10^{6} and B = 51,000.

1935

Shun-ichi Satô (35) determined the heat of formation from the dissociation pressure of boron nitride and the specific heats of boron, nitrogen, and BN as follows: $2\,BN \rightarrow 2B + N_2$ - 56,940 cals., with the heat of formation equal to minus-28,470 calories per mole. ΔF^{o}_{2980} was calculated as minus-27,380 calories per mole (compare Slade and Higson (20) 1919; Lorenz and Woolcock (33) 1928).

1936

Schaller (36) investigated volcanological boron compounds and found that recorded evidence indicated that boric acid, ammonium borates, alkali borofluorides, and sodium borate are the only boron compounds present. There was no evidence of natural boron nitride reported.

Kratky (37) patented a process for producing boron nitride. It consisted of pressing a porous bar of boron and then heating it for a suitable period of time at about 1,600° C. with a continuous supply of nitrogen. During nitrification, the bars were enveloped with an inert powder (for example, W or WC) to isolate them from the furnace or crucible walls.

1937

Shafran and Ormont (38) prepared boron nitride from H_3BO_3 by passing through the latter a stream of NH_3 and NH_4Cl at a temperature of about 1,200° C. and then subliming the NH_4Cl by continued blowing with NH_3 at 1,200° - 1,700° C.

Kelley (39) investigated the thermodynamic properties of boron nitride. For the formation of boron nitride from the elements according to the following equation: $B + 1/2N_2 = BN$, the following values were obtained: $\Delta H_{298.10}$ = minus-31,530 calories and $\Delta F^{o}_{298.10}$ = minus-27,690 calories (compare Shun-ichi Satô (35) 1935).

1938

The British Thomson-Houston Co., Ltd. (40), patented a process for producing boron nitride that consisted of passing gaseous NH_3 through a mixture of an oxygen-containing boron compound (for example, boric oxide, boric acid, pyroboric acid, or metaboric acid) and a diluent consisting of previously formed BN, while maintaining a temperature of 700° - 1,100° C.; this temperature range was conducive to full conversion of the mixture to boron nitride.

1940

Brager and Zhdanov (41) investigated the nature of the chemical bond in graphite and boron nitride by means of X-ray Fourier synthesis. They concluded that betweeen

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the layers of carbon atoms in graphite or boron and nitrogen atoms in boron nitride there is about 16 percent of the total electron density, which corresponds to 1 electron for every atom of carbon in graphite or 2 electrons for every pair of boron-nitrogen atoms in boron nitride. These electrons seem to cause the electrical conductivity of graphite. They also concluded that each layer of boron nitride consists approximately of B^- N^+ ions (the magnitude of the charges was not clear), each atom (ion) having an electronic configuration similar to that of carbon and therefore giving a structure analogous to that of graphite. The presence of ions in the layers was stated as the reason for absence of metallic conductivity in boron nitride.

Douglas and Herzberg (42) found two new bands in a discharge through helium containing traces of boron trichloride and nitrogen. The bands, a triplet and a singlet, were shown to be due to the BN molecule. The first band (triplet) represents an upper state-lower state transition similar to that shown by the C_2 molecule, to which BN is isoelectronic.

1941

Brill, Hermann, and Peters (43) questioned the accuracy of the results and conclusions of Brager and Zhdanov (41) in relation to the chemical bond in graphite and boron nitride.

1945

Foster and others (44) investigated the preparation of crucibles from boron nitride. Although the crucibles were somewhat porous, they had good insulating properties for high-temperature work. At 2,000° C., in vacuo, boron nitride began to sublime. It formed an alloy in contact with tungsten at 2,200° C. in an ammonia atmosphere. The BN crucibles were not wetted by molten iron or cerium but were attacked extensively by molten beryllium. Hydrostatic pressing of the powder (with a binding additive, such as Carbowax 4000, if desired) in rubber molds proved very satisfactory. The green crucibles were given a preliminary low-temperature firing to volatilize the binder and were then fired at high temperature in an ammonia atmosphere. The boron nitride used was produced by the boric acid-calcium phosphate-ammonia method.

1949

Alexander (45) patented a process for manufacturing boron nitride. It consisted of placing a charge of the nitride-forming metal in a closed reaction chamber, evacuating the chamber, and heating the metal to maintain it above its minimum nitride-forming temperature but below its fusion point. Nitrogen and an inert gas were then admitted to the reaction zone in controlled quantities so as to limit the exothermic heat generated by the nitriding reaction and thus maintain the temperature below the fusion point of the metal.

1951

Kohn (46) emphasized the analogy between graphite and BN and pointed out the theoretical possibility for a BN of sphalerite-type structure. He stated that attempts at a synthesis of such a hard form of BN would serve as an approach to the synthesis of the diamond itself.

An anonymous article published in Chemical Industries Week (47) described some of the physical and chemical properties of boron nitride and some of its applications. The latter included its use as an antisticking lubricant in glassmaking molds and its use in Ignitron ignitors. The article also discussed its reaction with carbon at 2,000° C. to form boron carbide and nitrogen, in contrast to its apparent inertness to CO at that temperature, and its stability as a refractory in electrical induction heating.

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Finlay and Fetterley (48) discussed the history, principle methods of production, chemical, physical, and optical properties, and known and potential uses of boron nitride. They included a description of a high-purity boron nitride, which the Norton Co. is producing; analysis showed 43.74 percent boron and 55.26 percent nitrogen (compared with the theoretical values of 43.6 percent B and 56.4 percent N). It is produced as fine, white, hexagonal crystal flakes with an average diameter of 1 micron. Occasional thin flakes up to 20 microns in diameter and rodlike crystals 0.5 micron in diameter and up to 20 microns long have been observed. The method used to produce this high-purity product was not disclosed.

Evans (49) attempted to develop an economical method of producing pure, stable boron nitride. Preliminary investigations utilizing electrothermal methods were carried out. A fair grade of BN was obtained from the vapor-phase reaction between B_2O_3 and NH_3. Briquets made of a mixture of NH_4Cl and B_2O_3, placed in silica crucibles and heated to 1,000° - 1,600° C. in an atmosphere of helium, proved unsatisfactory for production of BN.

1952

Evans (50) continued his investigations on boron nitride. Fluffy BN-NH_4Cl, from a BCl_3 and NH_3 reaction at 500° C., was pressed into briquets and heated to 1,000° C. in an atmosphere of NH_3 and N_2 in a Globar furnace. The NH_4Cl was volatilized, and the residue consisted of a stable BN product analyzing 55.0 percent nitrogen against the theoretical value of 56.4 percent. Another test involved heating boron aminochloride plus ammonium chloride briquets to 1,700° and 1,800° C. in a helium atmosphere. The BN residue contained 55.4 and 54.6 percent nitrogen, respectively. This represents a 98.2 and 96.8 percent pure boron nitride. The reaction product at 1,700° C. was almost pure white but contained 1.04 percent carbon and 1.94 percent soluble boron, whereas the product at 1,800° C. was grayish and contained 1.38 percent carbon and 0.56 percent soluble boron.

Pease (51) made an X-ray study of boron nitride which was recrystallized by heating at 2,050° C. for about 2 hours in a stream of nitrogen. The product appeared to be similar to that described by Goldschmidt (30). CuK and MnK radiations were used on powder samples. The reflection planes were indexed on the basis of a bimolecular, hexagonal unit cell with $a_o = 2.50399 \pm 0.00005$A. and $c_o = 6.6612 \pm 0.0005$A. at 35° C., assuming CuK $\alpha_1 = 1.54051$A. All reflections with $h + 2k = 3n$ and ℓ odd were absent. The structure (space group $C6_3mc$) was shown to be a simple layer type with interplanar spacings of $1/2c$, each layer consisting of a flat or nearly flat network of B_3N_3 hexagons. The positions of the boron atoms were calculated as (0, 0, 1/2) and (1/3, 2/3, 0), and for the nitrogen atoms (0, 0, 0) and (1/3, 2/3, 1/2). Thus, the hexagonal rings are packed directly on top of one another, whereas in graphite a form of close packing exists in which half of the atoms lie between the centers of the hexagonal rings of adjacent layers. No form of boron nitride was found that was similar to the rhombohedral modification of β-graphite. The structure found for BN is related to the wurtzite structure in the same way as the structure of graphite is related to that of the diamond. The nitrides of the other elements of the same subgroup of the periodic table (AlN, GaN, InN) have the wurtzite structure. The B-N bond has an electrical dipole moment, and the difference in packing may be due to the interlayer attraction of these dipoles. Pease also states that the structure contains only one type of strong bond, the B-N bond joining each atom to its three coplanar nearest neighbors. Its length is 1.446A., whereas the sum of the single-bond covalent radii of boron and nitrogen is 1.58A. (Pauling (52).)

PHYSICAL PROPERTIES

Color: White (30), transparent to light (41); material contaminated with carbon is gray (28).

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Feel: Greasy, similar to talc (30).

Hardness: 1-2 on Mohs' scale (30).

Particle size: Varies from submicroscopic amorphous (30) to flakes up to 20 microns in diameter (48).

System and habit: Hexagonal, generally thin, flexible plates (30); however, Finlay and Fetterly (48) also reported rodlike crystals.

Unit cell dimensions: $a = 2.50399 \pm 0.0005$A., $c = 6.6612 \pm 0.0005$A., $c/a = 2.66$ (51) (at 35° C., assuming CuK $\alpha_1 = 1.54051$A.)

Cleavage: Good basal cleavage (30).

Calculated density: 2.270 as determined from X-ray data (51).

Observed density: 2.34 (28), 2.255 ± 0.02 (30), 2.29 ± 0.03 (51).

Refractive index: Above 1.74 (30).

Birefringence: About 0.3 (30).

Extinction direction: γ' parallel to the trace of the base (30).

Optical character: Uniaxial negative (hexagonal) (30).

Luminescence: Specimens containing carbon impurities luminesce between blue and yellow-green upon excitation (27).

Electrical resistivity: High at all temperatures (established as 1,900 ohm-cm. at 2,000° C.) (18).

Diamagnetic susceptibility: $k \times 10^{-6} = \pm 0$; k in c.g.s.e.m.u.g.$^{-1}$ (for unrecrystallized BN) (53). $k \times 10^{-6} = -0.4 \pm 0.1$; k in c.g.s.e.m.u.g.$^{-1}$ (for recrystallized BN (54).

Sublimation temperature: 3,000° C. at 760 mm. (55).

Melting point: Above 3,000° C. under pressure with nitrogen (56).

Equilibrium dissociation pressure: 158 mm. at 2,045° C. (33).

Thermal conductivity: Very low for the powder because of its low bulk density (48).

Thermal coefficients of expansion: (In the range 0° - 800° C., t in °C.; values in Angstroms.) c dimension expansion with increasing temperature equals $6.6515 + 2.74 \times 10^{-4}t$, and the mean coefficient is 40.5×10^{-6} deg^{-1}. a dimension contraction with increasing temperature equals $2.50424 - 7.42 \times 10^{-6}t + 4.79 \times 10^{-9}t^2$, with the mean coefficient of expansion -2.9×10^{-6} deg^{-1} at 20° C., falling to zero at 770° C. (51).

Specific heat equations: B: $Cp = 1.54 + 4.40 \times 10^{-3}$ T.
N_2: $Cp = 6.50 + 1.00 \times 10^{-3}$ T.
BN: $Cp = 3.22 + 8.00 \times 10^{-3}$ T.
$2\,BN = 2B + N_2$: $\Delta Cp = 3.14 - 6.20$ T.
(The above equations are not highly accurate and hold only for temperatures below 1,173° C.) (57).

$\Delta H_{298.1°} = -31,530$ calories (39).
$\Delta F°_{298.1°} = -27,690$ calories (39).

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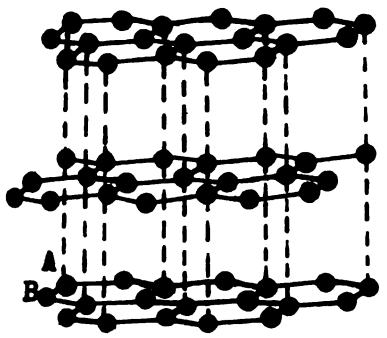

Fig. 1 (58)

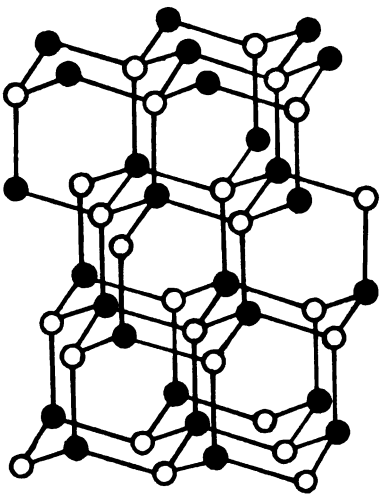

Fig. 2 (58)

Atomic Positions[4]

A: $(000, 00\frac{1}{2})$

B: $(\frac{1}{3}\ \frac{2}{3}\ u,\ \frac{2}{3}\ \frac{1}{3}\ u + \frac{1}{2})$[5]

Graphite (Structure shown)	BN (A = Nitrogen; B = Boron)
a_o = 2.456	a_o = 2.51
c_o = 6.796	c_o = 6.69
c/a = 2.77	c/a = 2.67
z = 4	z = 2

Atomic Positions

Zn: $(000,\ 0\ \frac{1}{2}\ \frac{1}{2},\ \frac{1}{2}\ 0\ \frac{1}{2},\ \frac{1}{2}\ \frac{1}{2}\ 0)$

S: $(\frac{1}{4}\ \frac{1}{4}\ \frac{1}{4},\ \frac{1}{4}\ \frac{3}{4}\ \frac{3}{4},\ \frac{3}{4}\ \frac{1}{4}\ \frac{3}{4},\ \frac{3}{4}\ \frac{3}{4}\ \frac{1}{4})$

Sphalerite (Structure shown)	Diamond
a_o = 5.42	a_o = 3.56
z = 4	z = 8

4/ All units are in Angstroms.

5/ Parameter u for graphite is practically zero and cannot exceed 0.05; u for BN is zero.

Figure 1 illustrates the structure of BN (identical with graphite, if all atomic positions are filled by C) according to Hassel (31) and Brager (59).

Figure 2 illustrates the sphalerite structure, and also, providing all atoms are the same, the diamond structure. It also represents the arrangement postulated for a cubic modification of boron nitride on the basis of Hassel's and Brager's BN structure. (46)

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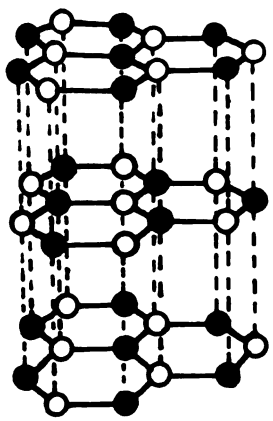

Fig. 3 (51)

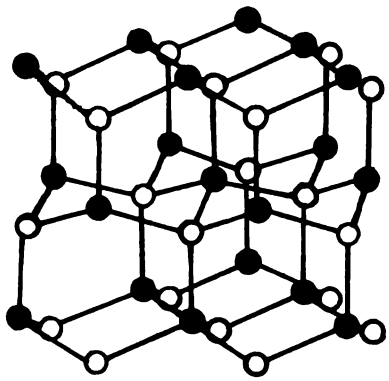

Fig. 4 (58)

Atomic Positions

N: $(000, \frac{1}{3}\frac{2}{3}\frac{1}{2})$

B: $(0\,0\,\frac{1}{2}, \frac{1}{3}\frac{2}{3}\,0)$

BN $a_o = 2.504$
$c_o = 6.662$
$c/a = 2.66$
$z = 2$

Atomic Positions

Zn: $(\frac{1}{3}\frac{2}{3}\,0, \frac{2}{3}\frac{1}{3}\frac{1}{2})$

S: $(\frac{1}{3}\frac{2}{3}\,u, \frac{2}{3}\frac{1}{3}\,u + \frac{1}{2})$

Wurtzite $a_o = 3.84$
$c_o = 6.28$
$z = 2$

Figure 3 illustrates the structure of boron nitride according to Pease (51).

Figure 4 illustrates the hexagonal wurtzite structure related to the boron nitride structure of Pease.

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CHEMICAL PROPERTIES

The chemical stability of boron nitride depends on the temperature at which it is produced or on the temperature to which it is later heated. That produced by Stock and Blix (9) at 130° C. was easily decomposed by moisture. Meyer and Zappner (22) found that BN produced at about 800° C. began to decompose after being exposed to air for a period of time, whereas that heated to about 1,000° C. showed only slight signs of decomposition after a long period of exposure to air. Friederich and Sittig (28) made boron nitride that was heated to 1,250° C. and found that it was not attacked by boiling water or a caustic-soda solution; however, it was decomposed by molten KOH.

At red heat oxidizing agents such as H_2O, CO_2, or O_2 will oxidize boron nitride to N_2 and B_2O_3; however, with the proper atmosphere it is an excellent refractory. In hydrogen it may be worked above 2,000° C. without decomposition; in ammonia or nitrogen higher temperature limits are permissible; for example, Podszus (56) reported that it is refractory at 3,000° C. in nitrogen. Upon extensive boiling with water or acid solutions, boron nitride hydrolyzes to NH_3 and boric acid.

Moeser and Eidmann (11) reported the following chemical reactions for boron nitride produced at the temperature of a gas-blast oven: Insoluble in water; slowly decomposable by boiling water; slight decomposition in water at ordinary temperatures; slight reduction of SO_2 with precipitation of sulfur upon heating BN with SO_2; heating with CO_2 resulted in reduction to CO; heating in NH_4F in an excess of concentrated sulfuric acid resulted in complete decomposition with the formation of ammonium sulfate and volatile BF_3; the oxides of arsenic, antimony, bismuth, and cadmium were reduced to their metal with simultaneous formation of the borate and nitric oxide; ferric and zinc oxides were not reduced; molybdenum trioxide was partly reduced to the lower blue oxide; chromic trioxide was reduced to chromous oxide; melting an excess of the alkali sulfates with BN reduced it to the metallic sulfide; slow melting of BN and sodium peroxide gave the borate and nitrate; and BN added to molten sodium peroxide gave the oxidation products of the borate and nitrogen. Wöhler (4) and Darmstadt (7) both reported that chlorine attacks boron nitride at high temperatures, forming BCl_3. Wöhler found that lead, mercuric, and copper oxides were also reduced to the metals, with the formation of nitric oxide. At 2,000° C. boron nitride reacts with carbon to form B_4C and N_2; however, it is stable to CO (47). At temperatures of about 3,000° K. 5 percent boron nitride mixed with 95 percent tungsten will melt, and the resulting boron alloys itself with the tungsten (28).

Impurities such as H_3BO_3, B_2O_3, C, Mg, Si, Ca, Al, Fe, and NH_4Cl have been observed in quantities ranging from mere traces to several percent. Finlay and Fetterley (48) reported that the purity of boron nitride on the present market ranges from 11 to 98 percent BN.

DISCUSSION

One of the most interesting facts about boron nitride is its resemblance to graphite, the soft, crystalline form of carbon. This similarity has been emphasized by the use of such terms as "white lampblack" and "white graphite" when referring to boron nitride. The two compounds are similar in crystal structure. Figure 1 illustrates the structure of BN (and also of graphite when all the atomic positions are filled by C) as reported by Hassell (31) and Brager (59). However, Pease (51) showed recently that, although the structure of boron nitride is similar to graphite, there is a geometrical difference in the nature of the layer stacking (see fig. 3). Whereas

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in graphite the layers are horizontally displaced so that half of the atoms lie between the centers of the hexagonal rings of adjacent layers, in boron nitride the hexagonal rings are stacked directly on top of each other, that is, with no horizontal displacement.

The supposedly isostructural relation of boron nitride to graphite led such investigators as Boeseken (24), Grimm and Sommerfeld (29), Goldschmidt (30), and Kohn (46) to consider the possibility of finding or synthesizing a cubic, diamond-like (actually sphaleritelike) form of BN that might rival the diamond in hardness. The structure of such a compound would be similar to that illustrated in figure 2. That its hardness might be expected to approach that of the diamond may be inferred from a comparison of the B-N interatomic distance with that of C-C in graphite (1.446A. (51), as compared to 1.42A. (58)), and by the sum of the single-bond covalent radii of B-N, as compared with that of C-C (1.58A. (52) to 1.54A. (52)). Kohn has pointed out (personal communication) that if Pease's interpretation of the structure of the hexagonal form of boron nitride is correct, then the structure of its postulated hard modification, if such is possible, would be that of wurtzite, as illustrated in figure 4. As the interatomic distance in the wurtzite-type structure would be expected to be slightly greater than in the sphalerite-type structure, because the ratio of ionic to covalent bonding is greater in the former, it probably would not be quite as hard. Nevertheless, it still might prove harder than any known compound, except the diamond itself.

Returning from the realm of speculation, is there any evidence to date that might indicate the existence of a cubic modification of boron nitride? A naturally occurring form of the compound has never been found (36). Of the many methods developed for producing boron nitride, all but a few have yielded nothing but an amorphous-powder product. For example, Goldschmidt (30) obtained single crystals up to 3 microns in diameter of a soft, hexagonal form of BN by recrystallizing the amorphous powder at approximately 2,500° C. More recently, Finlay and Fetterley (48) prepared single crystals of the same hexagonal form up to 20 microns in diameter; their method of production was not disclosed. In no instance has the existence of a hard modification of boron nitride been verified. Nevertheless, the possibility of the existence of such a compound is alluring enough to encourage attempts at its synthesis.

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